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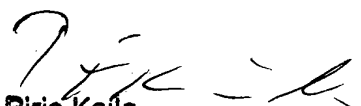
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Keksinnön nimitys  
Title of invention

"Process for producing aluminium oxide films at low temperatures"  
(Prosessi alumiinioksidiohutkalvojen valmistamiseksi matalassa  
lämpötilassa)

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## PROCESS FOR PRODUCING ALUMINIUM OXIDE FILMS AT LOW TEMPERATURES

### Background of the Invention

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#### Field of the Invention

The present invention concerns a process for producing aluminium oxide films by an ALD type process. According to the present process the aluminium oxide films are produced at  
10 low temperatures by bonding a metal compound on a substrate and converting said metal compound into a metal oxide.

#### Description of Related Art

15 Dielectric thin films having a high dielectric constant (permittivity) are used in various applications in the field of micro electronics. For example, the  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  presently used in DRAM-memories will have to be replaced with materials having higher dielectric constants as the size of the capacitors is decreasing while the capacitance has to remain constant.

20

$\text{Al}_2\text{O}_3$  films suitable for passivating surfaces have previously been prepared by physical processes, such as sputtering. The problem of the films produced by sputtering has been the unevenness of the formed film, and the pin holes remaining in the film, said pinholes forming a diffusion path for water through the film.

25

Dautartas and Manchanda have disclosed a method to reduce carbon contamination of  $\text{Al}_2\text{O}_3$  thin films. The applied process is an ALD type process and organic aluminium precursors are used together with water. Ozone is introduced into the reaction chamber to reduce carbon contaminants at least every third cycle. The process has its limits since  
30 aluminium oxide films deposited below  $190^\circ\text{C}$  were not dense and reproducible.

(Mindaugas F. Dautartas and Lalita Manchanda, US 6,124,158)

An ALD type method has also been used for producing  $\text{Al}_2\text{O}_3$  films by using aluminium alkoxides, trimethyl aluminium (TMA) or  $\text{AlCl}_3$  as the aluminium source material and

water, alcohols,  $\text{H}_2\text{O}_2$  or  $\text{N}_2\text{O}$  as the oxygen source material.  $\text{Al}_2\text{O}_3$  films from TMA and water have been deposited at a temperature in the range from 150 to 400 °C; typically the temperature has been 150 to 300 °C. The obtained ALD films have had uniform thickness and have not contained any pin holes, although the density of the film has been

5 questionable at the lower end of the deposition temperature range. In applications using organic polymers or low molecular weight organic molecules, such as organic EL displays, the deposition temperature, however, needs to be preferably under 150 °C. In cases where the substrate used is sensitive to water, it is impossible to use water as the oxygen source material.

10

### Summary of the Invention

The present invention is based on the surprising finding that high-quality aluminium oxide thin film can be grown by an ALD type process at substrate temperatures down to 100 °C.

15 Another surprising finding was that ozone could be used in the deposition process without destroying the properties of substrates that contained an organic layer. A dense pinhole-free thin film layer can be obtained very quickly by ALD on the substrate surface which protects the sensitive materials underneath the surface against the surrounding gas atmosphere.

20

More specifically, the present process is characterised by what is stated in the characterising part of claim 1.

A number of considerable advantages is obtained by means of the present invention. Thus, 25 with the aid of the present invention, it is possible to produce films of good quality at low temperatures.

The dielectric thin films having a dense structure can be used for passivating surfaces that do not endure high temperatures. Such surfaces are, for example, polymer films. Further, if 30 a water-free oxygen source is used, also surfaces that are sensitive to water can be passivated.

In addition, dielectric films including aluminium oxide with a dense structure can be used as buffer layers between functional films that include at least one organic film. The dielectric film then prevents either reaction or diffusion between the functional films.

## 5 Brief Description of the Figures

Figure 1 depicts in a schematic manner a cross-section of an organic EL display which is sealed against surrounding gas atmosphere with a passivating layer; and

Figure 2 depicts a structure of a SAW (Surface Acoustic Wave) filter.

10

## Detailed Description of the Invention

### **Definitions**

For the purpose of the present invention, an "ALD type process" designates a process in which deposition of thin film from gaseous source chemicals onto a surface is based on sequential self-saturating surface reactions. The principles of ALD process is disclosed, e.g., in US 6,015,590.

"Reaction space" is used to designate a reactor or reaction chamber in which the conditions can be adjusted so that the deposition by ALD is possible.

"Thin film" is used to designate a film which is grown from elements or compounds that are transported as separate ions, atoms or molecules via vacuum, gaseous phase or liquid phase from the source to the substrate. The thickness of the film depends on the application and it varies in a wide range, e.g., from one molecular layer up to 1000 nm, or even more.

By "dense" structure is meant a thin film which has a smaller leakage current through it or which has a lower permeability to ions or gases when comparing two thin films consisting essentially of the same basic material.

### **The deposition process**

An aluminium oxide thin film functioning as a dielectric or a passivating layer is grown on a desired substrate by ALD. The substrate is heated to the processing temperature which is preferably selected from a range of about 100 °C - 190 °C.

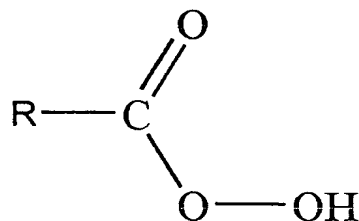
In particular, the following organoaluminium compounds containing at least one alkyl group bound to aluminium are used in the present invention:

- 5        - Monoalkyl aluminium compounds  $L^1AlX_2$ , wherein X is selected from a group H, F, Cl, Br, I, RCHO, wherein RCHO is an alkoxy group and  $L^1$  is a linear or branched hydrocarbon that is saturated or unsaturated.
- Dialkyl aluminium compounds  $L^1L^2AlX$ , wherein X is selected from a group H, F, Cl, Br, I, RCHO, wherein RCHO is an alkoxy ligand and  $L^1$ ,  $L^2$  are linear or
- 10       branched hydrocarbons with single, double and/or triple bonds.
- Trialkyl aluminium compounds  $L^1L^2L^3Al$ , wherein  $L^1$ ,  $L^2$  and  $L^3$  are linear or branched hydrocarbons with single, double and/or triple bonds.

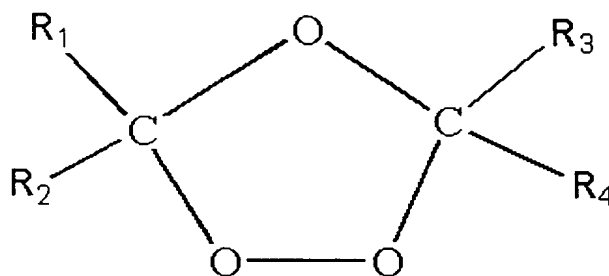
15       The organoaluminium compound is introduced into the reaction chamber in gaseous phase and contacted with the substrate surface.

Most preferably trimethyl aluminium  $(CH_3)_3Al$ , also known as TMA, is used as the aluminium source chemical.

- 20       Strongly oxidizing source chemicals containing oxygen are used in the process. As an oxygen source, one or several chemicals selected from the following group is used: ozone, organic ozonides, oxygen atoms containing unpaired electrons, organic peroxides and organic peracids.



- 25       Peracids, such as peracetic acid  $CH_3COOOH$ , contain OOH and O groups bound to the same carbon atom.



Organic ozonides contain both O and O-O groups between two carbon atoms.

5

Dimethyl peroxide and benzoyl peroxide are examples of suitable organic peroxides. In addition to these said compounds, the peroxide can be one of the following compounds:  $R^1-O-O-R^2$ , wherein  $R^1$  and  $R^2$  are linear, branched or cyclic organic ligands such as  $CH_3$ ,  $(CH_3)_3C$ ,  $C_6H_5$  or benzoyl

10 or

$R^1-O-O-H$ , wherein  $R^1$  is a linear, branched or cyclic organic ligand such as  $CH_3$ ,  $(CH_3)_3C$  or  $C_6H_5$

Most preferably ozone is used as an oxygen source.

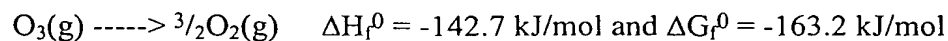
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Water is not used as a source chemical in the deposition process. The obtained growth rate of aluminium oxide is as good as around  $0.8 \text{ \AA/cycle}$ . It is assumed that the surface reactions between ozone and trimethyl aluminium or fractions of trimethyl aluminium bound to surface, such as dimethyl aluminium and monomethyl aluminium, provide enough OH groups on the aluminium oxide surface for the self-saturating chemisorption reaction of the following trimethyl aluminium pulse with the substrate surface.

20

Ozone is not only an oxygen source for the process but it also contains a lot of chemical energy which is released when the molecule is broken.

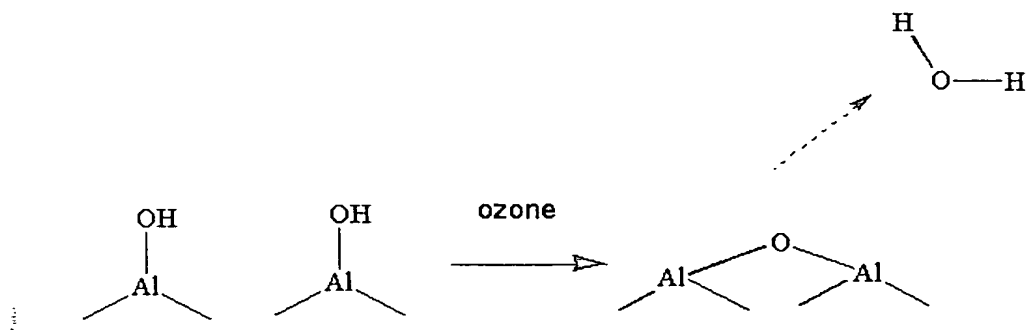
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(N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements", Pergamon Press Ltd., Oxford, England 1986.)

Break up of ozone molecules can provide additional energy to the top molecular layers of surfaces and thus promote some surface reactions. The densification of  $\text{Al}_2\text{O}_3$  surface may proceed via elimination of surplus OH groups and formation of Al-O-Al bridges.

5



Also when the O-O bond of an organic peroxide breaks, the resulting RO fragments are highly reactive.

10

Before introducing ozone to the reaction chamber, ozone is optionally diluted. In this purpose oxygen gas, inert gases such as nitrogen or noble gases such as argon can be used.

15

Examples of applications for which the aluminium oxide films prepared according to the present process are particularly suitable are organic light-emitting diodes (OLED), organic electroluminescent displays (OEL), organic solar cells (OSC) and surface acoustic wave (SAW) filters. These applications generally require a low deposition temperature and/or are sensitive to moisture and/or oxygen.

20

According to a first preferred embodiment of the present invention, an organic EL display including a passivating layer is produced. A typical organic EL display is produced by arranging on a substrate 11 (cf. Figure 1), which typically is made of glass or corresponding material, an anode 12. On the anode 12 there is deposited a hole transport layer 13, and an emission layer 14 is deposited on said hole transport layer 13. Further, on the emission layer 14 there is deposited layer 15 capable of transporting electrons. All these layers 13 – 15 preferably comprise organic material, the said organic material being either a polymer or low molecular weight molecules. On the layer 15 capable of

25

transporting electrons is then arranged a cathode 16. The cathode is made of a metal which is typically aluminium, magnesium or calcium-coated aluminium. The said metals easily acquire an oxide layer on the metal surface which is detrimental to the interface between the metal and the organic layer. A passivating layer 17 is then produced onto the surfaces  
5 of the thus obtained structure by the present process. It is to be noted that by "surfaces" is meant all the possible surfaces, i.e., also vertical surfaces are preferably passivated.

According to a second preferred embodiment of the present invention, a SAW filter containing a protective layer is produced. A typical SAW filter is presented in Figure 2. It  
10 comprises a first acoustic absorber 21 and a second acoustic absorber 22 placed on a piezoelectric substrate, the said piezoelectric substrate typically being quartz, lithium niobate or lithium tantalate. The coming signal is conducted to an input transducer 23 and the leaving signal is collected from an output transducer 24. The input transducer converts electrical signals to small acoustic waves, the said acoustic waves being reconverted to  
15 electrical signals by the output transducer. Usually the structure is hermetically encapsulated. The present invention replaces the hermetical encapsulation with a thin protective layer that is deposited on the surface of the SAW structure by the present process. Thus, a cheaper encapsulation process can be applied to the protected structure to obtain a finished SAW product.

20 Single wafer reactors, reactors with multiple wafers or other substrates in a planar or vertical substrate holder and a batch process reactor serve as examples of the ALD reactor types where this low-temperature process invention can be utilised. Organic solar cells are coated with the protective layer preferably in a batch process reactor to keep the  
25 manufacturing costs / substrate low.

The invention is further illustrated with the aid of the following non-limiting working examples.



**Example 1: Depositing  $\text{Al}_2\text{O}_3$  thin films using either water or ozone as an oxygen source**

**Case A: Deposition of  $\text{Al}_2\text{O}_3$  films with water as an oxygen source**

- 5  $\text{Al}_2\text{O}_3$  thin films were deposited in a flow-type ALD reactor, model F-120, manufactured by ASM Microchemistry Oy, Finland. Trimethyl aluminium  $(\text{CH}_3)_3\text{Al}$ , also known as TMA, was used as an aluminium source chemical. Purified water was used as an oxygen source chemical. The source chemicals were introduced from external sources to the reactor.
- 10 A substrate was provided to the reaction space and the reactor was evacuated to vacuum with a mechanical vacuum pump. Next, the pressure of the reaction space was adjusted approximately to a range of 5 - 10 mbar with flowing nitrogen gas. Then the reaction space was heated to the deposition temperature.
- 15 The thin films were deposited at 100 °C and 300 °C. The source chemicals were pulsed into the reaction space according to the principles of ALD, i.e. the pulses were separated from each other with inert gas to prevent mixing of the source chemicals in the gas phase of the reaction space. Only surface reactions were allowed to occur.
- 20 The pulsing cycle was as follows:
- TMA pulse 0.5 s
  - $\text{N}_2$  purge 1.0 s
  - $\text{H}_2\text{O}$  pulse 0.4 s
  - $\text{N}_2$  purge 1.5 s
- 25 The growth rate of  $\text{Al}_2\text{O}_3$  from TMA and  $\text{H}_2\text{O}$  was 0.8 Å/cycle at 300 °C and 0.5 Å/cycle at 100 °C. The refractive index was 1.64 for the film grown at 300 °C and 1.59 for the film grown at 100 °C. The films grown at 100 °C started to leak immediately in the electrical measurements, and it was impossible to measure exact values for capacitance or breakdown voltage. It appeared that the films were not very dense.

30

**Case B: Deposition of  $\text{Al}_2\text{O}_3$  film with ozone as an oxygen source.**

$\text{Al}_2\text{O}_3$  thin films were deposited in a flow-type ALD reactor, model F-120, manufactured by ASM Microchemistry Oy, Finland. Trimethyl aluminium  $(\text{CH}_3)_3\text{Al}$ , also known as

TMA was used as an aluminium source chemical. Ozone prepared on the premises was used as an oxygen source chemical. The source chemicals were introduced from external sources to the reactor.

- 5 A substrate was provided to the reaction space and the reactor was evacuated to vacuum with a mechanical vacuum pump. Next, the pressure of the reaction space was adjusted approximately to a range of 5 - 10 mbar with flowing nitrogen gas. Then the reaction space was heated to the deposition temperature.
- 10 The thin films were deposited at 100 °C and 300 °C. The source chemicals were pulsed into the reaction space according to the principles of ALD as in case A.

The pulsing cycle was as follows: TMA pulse 0.5 s

N<sub>2</sub> purge 1.0 s

15

O<sub>3</sub> pulse 4.0 s

N<sub>2</sub> purge 1.5 s

As a summary, the resulting thin films had the following properties.

	Case B	Case B	Case A	Case A
Deposition temperature	100 °C	300 °C	100 °C	300 °C
Growth rate (Å/cycle)	0.8	0.8	0.5	0.8
Refractive index	1.58	1.66	1.59	1.64
Dielectric constant	6.0	8.3	*	
Breakdown voltage (MV/cm)	4.5	6.0	*	

20

\* The measurement could not be carried out due to electrically very leaky thin film.

A TOF-ERDA analysis of the film grown from TMA and ozone at 100 °C revealed that the film contained 6.0% of carbon and 15.8% of hydrogen.

25

A comparison between cases A and B shows that replacing water with ozone was beneficial for the deposition process at low temperature.

**Example 2: Depositing  $\text{Al}_2\text{O}_3$  thin films on an organic layer using ozone as an oxygen source**

5  
A substrate with an organic thin film was provided into the reaction space of an F-450 ALD reactor manufactured by ASM Microchemistry Oy, Finland. The pressure of the reaction space was adjusted to about 5 - 10 mbar with a mechanical vacuum pump and  
10 flowing nitrogen gas that had a claimed purity of 99.9999%. Then the temperature of the reaction space was adjusted to about 110 °C. TMA evaporated from an external source and ozone prepared on the premises were alternately introduced into the reaction space and contacted with the surface, the pulsing times being 1 s for TMA and 4 s for  $\text{O}_3$ . The source chemical pulses were separated from each other with nitrogen gas. The purging time lasted  
15 for 1.0 - 1.5 s after each source chemical pulse. The pulsing cycle consisting of these two source chemical pulses and two purging periods was repeated until a 50-nm aluminium oxide thin film was obtained on the substrate. Typically, around 600 pulsing cycles were needed for the deposition. As a result, the organic layer had not suffered from the deposition process. Further, the passivated structure could be stored at ordinary room air  
20 without destroying the functionality of the organic layer.

## Claims

1. Process for producing aluminium oxide thin films on a substrate by using the ALD method, according to which process
  - 5 - a vaporizable organoaluminium compound is bonded to a growth substrate, and
  - the bonded organoaluminium compound is converted to aluminium oxide, characterised in that
    - the bonded organoaluminium compound is converted to aluminium oxide by contacting it with a reactive vapour source of oxygen other than water, and
    - 10 - the substrate is maintained at a temperature of less than 190 °C during the growth process.
2. The process according to claim 1, wherein the vaporizable organoaluminium compound contains at least one alkyl group bound to aluminium.
3. The process according to claim 1 or 2, wherein the formula of the vaporizable organoaluminium compound is
  - 15  $L^1AlX_2$  (I)
  - or  $L^1L^2AlX$  (II)
  - or  $L^1L^2L^3Al$  (III)

wherein X is selected from a group H, F, Cl, B, I, RCHO

20 wherein RCHO is an alkoxy group, and

$L^1$ ,  $L^2$  and  $L^3$  are linear or branched, saturated or unsaturated hydrocarbons.
4. The process according to any of the preceding claim, wherein the reactive source of oxygen is ozone, an organic ozonide, oxygen atoms with unpaired electrons, an organic peroxide, organic peracids or a mixture or a combination of two or more of them.
- 25 5. The process according to any of the preceding claim, wherein the reactive source of oxygen contains one or more organic peroxides with a formula
 
$$R^1-O-O-R^2 \quad (IV)$$

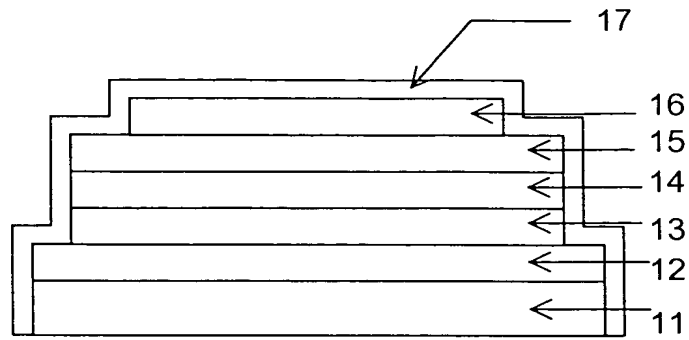
wherein  $R^1$  is a linear, branched or cyclic organic ligand, and

30 wherein  $R^2$  is a hydrogen or a linear, branched or cyclic organic ligand.

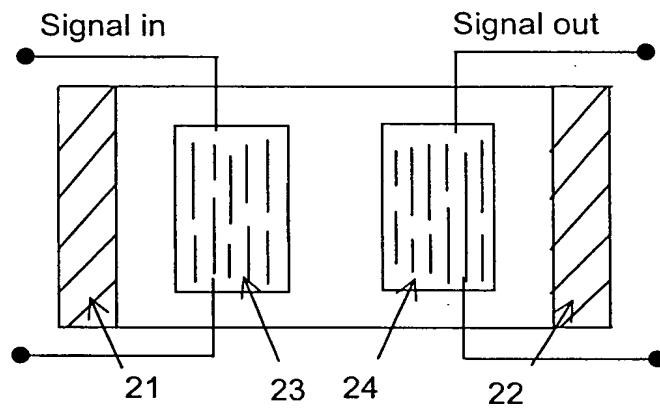
6. The process according to any of the preceding claims, wherein the substrate is preferably maintained at a temperature of less than 160 °C during the process.
7. The process according to any of the preceding claims, wherein the substrate is most preferably maintained at a temperature of less than 130 °C during the process.
- 5 8. The process according to claim 1, wherein the thickness of the aluminium oxide film is approximately 5 - 1000 nm.
9. The process according to claim 8, wherein the thickness of the aluminium oxide film is 25 - 75 nm.
- 10 10. The process in accordance with any of the preceding claims, wherein the substrate contains an organic light emitting layer.
11. The process in accordance with any of the preceding claims, wherein the substrate contains a surface acoustic wave filter.
12. The process in accordance with any of the preceding claims, wherein the substrate contains an organic solar cell layer.
- 15 13. A substrate containing material sensitive to moisture or other gaseous or liquid material in the surrounding atmosphere having formed thereon an aluminium oxide layer as an individual protective layer by the process of claim 1.
- 20 14. A substrate containing material sensitive to moisture or other gaseous or liquid material in the surrounding atmosphere having formed thereon an aluminium oxide layer by the process of claim 1 as a complementary protective layer on another layer of same kind deposited by another deposition process, such as CVD or PVD.

## (57) Abstract

- A process for producing aluminium oxide thin films on a substrate by the ALD method comprises the steps of bonding a vaporizable organoaluminium compound to a growth
- 5 substrate, and converting the bonded organoaluminium compound to aluminium oxide. According to the invention the bonded organoaluminium compound is converted to aluminium oxide by contacting it with a reactive vapour source of oxygen other than water, and the substrate is kept at a temperature of less than 190 °C during the growth process. By means of the invention it is possible to produce films of good quality at low temperatures.
- 10 The dielectric thin films having a dense structure can be used for passivating surfaces that do not endure high temperatures. Such surfaces are, for example, polymer films. Further, when a water-free oxygen source is used, also surfaces that are sensitive to water can be passivated.



**Fig. 1**



**Fig. 2**